Chemical Engineering Journal 153 (2009) 43–49

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Reaction path of ethanol and acetic acid steam reforming over Ni–Zn–Al catalysts. Flow reactor studies

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ARTICLE INFO

Article history:
Received 17 December 2008
Received in revised form 28 May 2009
Accepted 1 June 2009

Keywords:
Ethanol steam reformin
Hydrogen production
Ni catalyst
Reaction mechanism
Pathway of reaction
Mechanism of reaction
Acetic acid steam reforming
Water gas shift equilibrium
Methane steam reforming equilibrium

ABSTRACT

Ethanol steam reforming (ESR) experiments have been performed in dilute conditions over a NiZnAl catalyst. Experiments have been performed by varying catalyst surface area, reactants flow rate, contact time, reactants feed composition and temperature. Acetic acid steam reforming experiments have also been performed. The data suggest that adsorbed acetaldehyde and acetic acid play an important role as intermediates of ESR, while also acetone may have a role in the ESR reaction. The key step for high hydrogen yield during ESR is represented by the evolution of acetate species, either towards decomposition giving rise to methane + CO_x, or to steam reforming to CO_2 and H_2. At high temperature hydrogen production depends on approaching methane steam reforming and reverse water gas shift equilibria. Ethylene end dimethylether are parallel products found at low conversion. With excess water acetaldehyde is not found among the products, and hydrogen yields as high as 95% have been obtained at 853 K.

1. Introduction

Hydrogen is mostly produced today through steam reforming of hydrocarbons, usually natural gas [1,2], performed at 1000–1200 K. The industrial catalysts are invariably based on Ni supported on an alumina-based carrier, usually stabilized by the presence of alkali and alkali earth cations. Carbon dioxide, sometimes used industrially but mostly vent, is the byproduct of this process, thus contributing to the greenhouse effect.

The steam reforming of renewable organic materials (such as “bioethanol” produced by fermentation of glucose-rich biomass) is an option to produce hydrogen without any increase of greenhouse gas concentration. The steam reforming of (bio)ethanol (ESR)

$$C_2H_5OH_g + 3H_2O_g \rightarrow 2CO_2 + 6H_2 \quad (1)$$

is a widely studied reaction, as summarized in some reviews [3–5], but is still not performed at the industrial level. Nickel is commonly employed as the active phase to realize ethanol steam reforming at least at high temperature. Catalysts based on metals other than nickel (such as cobalt and noble metals) present good performances, perhaps better than nickel (less methane formed [5]), for low temperature processes.

ESR is a quite complex reaction. In an earlier study, Therdthianwong et al. [6] concluded that ESR over Ni/Al_2O_3 is essentially the sequence of a water assisted ethanol cracking reaction (producing CH_4, CO_2 and H_2) followed by methane steam reforming (MSR) and water gas shift equilibria (WGS). In a very recent study, Deng et al. [7] working with a NiZnZr catalyst proposed the same reaction path but suggested that methanation can be relevant in lowering CO selectivity. According to Benito et al. [8] the reaction mechanism proceeds via ethanol dehydrogenation to obtain acetaldehyde which is transformed by a decarbonylation reaction to CH_4. Fatsikostas and Verykios [9] investigated the reaction path of ESR over Ni/Al_2O_3 and Ni/La_2O_3 catalysts using temperature programmed desorption (TPD) and temperature programmed reaction (TPR) measurements. Using a water-to-ethanol ratio of 2 for their TPR experiments these authors proposed a relevant role of adsorbed acetaldehyde for the reaction. Also Vaidya and Rodrigues [10] emphasized the role of acetaldehyde in decreasing hydrogen production, while according to Vieira Fajardo and Dias Probst [11] both acetaldehyde and ethylene are intermediates in ethanol steam reforming over Ni/Al_2O_3. Mas et al. [12] in a detailed kinetic study performed above 823 K evidenced competitivity between reactants and with methane in the reaction, as well as a overall reaction order

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doi:10.1016/j.cej.2009.06.002

with respect to ethanol lower than one. These authors did not find any acetaldehyde among the products, working with excess water (water-to-ethanol 5.5). In practice, it seems that the authors still not converged into a general opinion about reaction mechanism and path for ESR over Ni catalysts, and that many details are still under study.

According to our previous studies [13–16], acetaldehyde, methane and CO are the main byproducts that may limit hydrogen yield, while at low conversion several other byproducts such as ethylene, diethylether and acetic acid are formed. However, while acetaldehyde is a main product in the absence of water or with a water-to-ethanol stoichiometric feed ratio of 3 over different Ni catalysts, in excess of water it may even disappear among the products. We also proposed a central role of acetate species, detected spectroscopically, in the methane forming step. Ni–Zn–Al mixed oxides produced by calcination of hydrotalcite-like layered double hydroxide precursors were found to be excellent catalysts for ESR [15,16].

Acetic acid steam reforming [17,18] and decomposition [19] over Ni catalysts has also been the object of recent investigations. These reactions, that also may produce “renewable hydrogen” are relevant with respect to ESR because of the possible role of acetic acid as intermediate in it. In the present paper we report on our investigation intended to have additional information on ESR reaction path and mechanism over a Ni:Zn:Al catalyst with 49.6:21.7:28.7 atomic ratio. The flow reactor experiments have been extended from 575 K to near 1173 K.

2. Experimental

2.1. Preparation of catalysts

The hydrotalcite-like precursor with Ni:Zn:Al atomic ratios 49.6:21.7:28.7 (S_{BET} 43.3 m^2/g) has been prepared with the urea method [16,20]. The mixed oxide catalyst (S_{BET} 105.2 m^2/g) was obtained by heating the hydrotalcite precursor in air, at the rate of 8 K/min up to 973 K, and maintaining them at this temperature for 5 h. As discussed previously [20], while the precursor appeared (based on SEM, XRD and IR techniques) to be formed by monophasic lamellar hydrotalcite-like hydroxy-carbonate/nitrate, the mixed oxide, although retaining the lamellar morphology, is a mixture of NiO (rock-salt type), ZnO and a spinel phase. Part of the catalyst was also calcined at 1173 K, causing a slight decrease of surface area (S_{BET} 85.2 m^2/g).

2.2. Catalytic tests

The catalytic experiments were carried out in a fixed-bed tubular quartz flow reactor, operating isothermally, loaded with 25 mg of catalyst mixed with 275 mg of quartz particles (both of them 60–70 mesh sieved). Products analysis was performed with a gas-chromatograph Agilent 4890 equipped with a Varian capillary column “Molsieve 5A/Porabond Q Tandem” and TCD and FID detectors in series. Between them a Nickel Catalyst Tube was employed to reduce CO to CH_4. A six-port valve with a 0.5 cm^3 loop was used for the gas sampling of the outlet gases.

The results reported are based on reactant conversions, selectivity to carbon-containing products and hydrogen yield vs. temperature. Reactant conversion is defined as usual:

$$C_R = 100\left(\frac{n_{R_{in}} - n_{R_{out}}}{n_{R_{in}}}\right)$$

where n_R is the number of reactant molecules (ethanol, acetic acid or water). Carbon-based selectivities to products is defined as follows:

$$S_P = 100.\frac{n_P}{(n_{R_{in}} - n_{R_{out}})(2/\nu_P)}$$

where ν_P is the number of carbon atoms in the product molecule. Yield to H_2 is defined as follows:

$$Y_{H_2} = 100\frac{n_{H_2\,out}}{x n_{R_{in}}}.$$

where x is 6 when R is ethanol or 4 when R is acetic acid..

3. Results

3.1. Catalytic activity tests in ESR

In Table 1, the results of ESR catalytic tests performed in different conditions are summarized. To have information on the possible role of gas-phase reaction, a blank experiment was done by feeding a 9.2:27.5:63.4 ethanol:water:N_2 mixture (water/ethanol molar ratio = 3) at 125 ml/min over a bed containing only 0.3 g of quartz, supposed to be inert. Ethanol conversion started to be significant above 700 K and almost total at 1062 K. However, water was not converted even at this temperature, being instead formed as a product. Ethylene is the main product with acetic acid and water at low temperature. At high temperature quite small amounts of CH_4 and CO and hydrogen started to be formed. Above 1000 K acetic acid selectivity dropped in favour of CH_4 and CO, formed with a molecular ratio near 1, while ethylene selectivity was quite stable above 20%. The yield in hydrogen was the higher, the higher the temperature, but no more than 16.3% at 1110 K.

When, in the same conditions, the same mixture was fed to a bed containing 0.27 g of quartz and 0.03 g of catalyst (experiment A), the situation was very different. Ethanol conversion started to be detectable already above 550 K and reaches ~100% at 770 K. To verify if our experimental conditions are significant to measure catalytic activity, we have measured the apparent activation energy for ethanol conversion assuming the hypothesis of a differential reactor at low conversion. We obtain 80 kJ/mol that actually indicate that, in our experimental conditions, the kinetics is, in the low temperature/low conversion range (conversion of ethanol < 20%, $T < 620$ K), limited by a “catalytic” chemical phenomenon. Water conversion (not shown) started to be significant only above 700 K, and reached a plateau at near 40% above 820 K. Below 620 K acetic acid was the main product. In the range 600–700 K, when ethanol conversion progressively approached to be total, acetaldehyde was produced in significant amount. Ethyl ether was also observed. However, above 673 K CH_4 (with selectivity decreasing by increasing temperature), CO (with selectivity increasing by increasing temperature), and CO_2 (with almost constant selectivity) were the predominant products.

The comparison of the results obtained with and without the catalyst show that, although the conversion of ethanol is not negligible in the non-catalytic reaction above 800 K, the products distribution is very different with respect to that obtained in the presence of the catalyst. On the other hand, ethylene produced by the thermal reaction could have some role in the catalytic behaviour in the high temperature range.

Experiment B has been performed just in the same conditions, as experiment A, but with the catalyst previously calcined at higher temperature (1173 K), thus resulting in lower surface area. The ethanol conversion curve is shifted to higher temperatures, as expected due to the decrease of surface area of the catalyst. Also the product selectivities change significantly. In particular, the selectivities to acetic acid and acetaldehyde are significantly increased in experiment B with respect to experiment A in the range below 853 K. At 853 K, more CO_2 and hydrogen and less CO and CH_4 are formed in experiment B with respect to experiment

Table 1
Ethanol conversion and selectivity to carbon products and yield to hydrogen upon ESR over NiZnAl catalyst.

Experimental	Thermal	A	B	C	D	E
He	(N_2) 63.4	(N_2) 63.4	(N_2) 63.4	83.3	85.2	85.2
C_2H_5OH	9.2	9.2	9.2	4.2	2.3	2.3
H_2O	27.5	27.5	27.5	12.5	12.5	12.5
ml/min	126	126	126	400	400	200
W_{cat}	0	0.03 g	0.03 g	0.03 g	0.03 g	0.015 g
S_{BET}, m^2/g	–	105	85	85	85	85
H_2O/EtOH	3	3	3	3	5.5	5.5
C_{EtOH}%						
$T = 573$ K	–	3.6	–	0	0	0
$T = 673$ K	0.1	55.3	12.3	4.2	7.6	14.8
$T = 723$ K	–	99.4	753 K, 99.5	16.2	24.6	60.6
$T = 773$ K	5.9	100		39.6	65.4	99.0
$T = 813$ K	–	100		85.0	95.1	100
$T = 853$ K	39.8	100	100	100	100	100
S_{CH_3COOH}%						
$T = 573$ K	–	86.3	–	–	–	–
$T = 673$ K	0	0	89.0	100	100.0	96.9
$T = 723$ K	–	0	753 K, 2.4	100	92.1	55.8
$T = 773$ K	57.2	0		90.0	77.7	0
$T = 813$ K	–	0		48.6	57.6	0
$T = 853$ K	38.6	0	4.7	0	0	0
S_{CH_3CHO}%						
$T = 573$ K	–	13.7	–	–	–	–
$T = 673$ K	0	7.1	11.0	0	0	0
$T = 723$ K	–	0	753 K, 1.9	0	0	0
$T = 773$ K	0	0		0	0	0
$T = 813$ K	–	0		0	0	0
$T = 853$ K	0	0	2.9	0	0	0
$S_{C_2H_4}$%						
$T = 573$ K	–	0	–	–	–	0
$T = 673$ K	100	0	0	0	0	3.0
$T = 723$ K	–	0	753 K, 0	0	7.9	2.6
$T = 773$ K	42.8	0		7.0	9.3	0
$T = 813$ K	–	0		11.5	13.7	0
$T = 853$ K	55.9	0	0	0	0	0
$S_{(CH_3CH_2)_2O}$%						
$T = 573$ K	–	0	–	–	–	–
$T = 673$ K	0	0	0	0	0	0
$T = 723$ K	–	2.9	753 K, 0.2	0	0	18.6
$T = 773$ K	0	0		0	3.8	0
$T = 813$ K	–	0		4.5	0	0
$T = 853$ K	1.5	0	0.2	0	0	0
$S_{CH_3COCH_3}$%						
$T = 573$ K	–	–	–	–	–	–
$T = 673$ K	0	0	0	0	0	0
$T = 723$ K	–	0	753 K, 0	0	0	12.2
$T = 773$ K	0	0		0	5.7	0
$T = 813$ K	–	0		3.1	0	0
$T = 853$ K	0	0	0	0	0	0
S_{CH_4}%						
$T = 573$ K	–	0	–	–	–	–
$T = 673$ K	0	72.1	0	0	0	0
$T = 723$ K	–	37.0	753 K, 43.7	0	0	1.0
$T = 773$ K	0	33.8		0.5	0.8	25.0
$T = 813$ K	–	25.0		4.7	7.3	11.4
$T = 853$ K	0.7	15.1	11.2	16.2	2.2	1.1
S_{CO}%						
$T = 573$ K	–	0	–	–	–	–
$T = 673$ K	0	15.6	0	0	0	0
$T = 723$ K	–	5.0	753 K, 29.1	0	0	1.4
$T = 773$ K	0	9.8		0.7	0.3	8.1
$T = 813$ K	–	15.7		14.4	1.9	13.6
$T = 853$ K	1.6	28.9	14.8	29.7	4.8	7.2
S_{CO_2}%						
$T = 573$ K	–	0	–	–	–	–
$T = 673$ K	0	5.1	0	0	0	0
$T = 723$ K	–	55.1	753 K, 22.6	0	0	8.5
$T = 773$ K	0	56.4		1.7	2.4	66.9
$T = 813$ K	–	59.3		13.2	19.5	75.0
$T = 853$ K	1.7	56.0	66.2	54.1	93.0	91.6

Table 1 (*Continued*)

Experimental	Thermal	A	B	C	D	E
Y_{H_2} %						
$T = 573$ K	–	1	–	0	0	–
$T = 673$ K	0	15.9	3.9	1.4	0	4.8
$T = 723$ K	–	50.6	753 K, 29.7	5.7	0	18.3
$T = 773$ K	1.1	51.7		12.5	18.8	50.2
$T = 813$ K	–	61.4		31.0	31.2	73.5
$T = 853$ K	5.1	70.2	73.3	67.5	95.4	96.1

A. This behaviour would indicate that CO is the end product, with CH_4, CO_2 and CH_3CHO being earlier products, being formed more with the lower surface area catalyst. The lower hydrogen yield at 853 K in the case of experiment A should essentially be due to the reverse-WGS reaction that converts CO_2 and H_2 into CO and water that would proceeds more efficiently towards equilibrium with the higher surface area catalyst.

We now compare the data concerning experiment C with those concerning the experiment A. In both cases the water-to-ethanol ratio is 3, and the catalyst is the same but in experiment A the feed flow rate is definitely higher and the contact time and the reactants concentration are lower. As expected, the conversion at low temperature in experiment C is lower than in experiment A, and the formation of acetic acid is definitely higher in the temperature range between 700 and 850 K. Ethylene was found as a significant product only at 773 and 813 K, when also diethylether and acetone were observed among the products. Acetaldehyde is not observed in experiment C. Methane starts to be observed at 773 K and increases in selectivity until 853 K, while also CO and CO_2 are produced in increasing amounts. As a result of this, the yield to hydrogen increases with temperature too, in this temperature range.

In experiment D, the total flow rate was not changed with respect to experiment C, but the water-to-ethanol molar ratio was increased to 5.5 by decreasing the ethanol partial pressure, without changing the water partial pressure. In spite of the decrease of the ethanol partial pressure, its conversion increases significantly. This would suggest that the kinetics of ethanol conversion to acetic acid, which predominates at low temperature, has a negative reaction order with respect to ethanol concentration. The products observed are the same as for experiment C, but their production is essentially shifted to lower temperature. At higher temperatures, however, methane and CO selectivities decrease significantly, in favour of CO_2 and H_2 formation. This is likely an effect of the decreased concentration of ethanol, which gives rise to a decreased concentration of methane and CO as intermediates (being water concentration constant), thus favouring their conversion into CO_2 and H_2 through water gas shift and methane steam reforming.

In the case of experiment E, the ethanol partial pressure was not changed, water concentration was still kept in excess and contact time was the same with respect to experiment D. However, both the reactants flow rate and the catalyst weight were decreased by half. Ethanol conversion increased further significantly, while the drop of the selectivity to acetic acid was observed at lower temperature, in favour of both diethylether and acetone at 720 K, and of CO, CO_2 and CH_4 at 770 K. These data can be tentatively interpreted assuming that ethanol conversion to both acetic acid and diethylether could be influenced by external diffusion phenomena under these conditions [21]. As said above, ethanol conversion to acetic acid, which predominates at $T \leq 720$ K, should have negative reaction order with respect to ethanol and could have positive reaction order with respect to water. On the contrary, diethylether formation may have negative reaction order with respect to water, as found for ether formation on alumina [22]. The increase of the reactants flow rate would result in an increase of the surface concentration of both reactants. The increased concentration of water could favour acetic acid formation while the decrease of reactants flow rate could result in a decreased surface water concentration thus limiting acetic acid formation rate and favouring diethylether formation [23].

The strong increase in the selectivities to CO, CO_2 and CH_4 at 773 and 814 K by decreasing reactants flow rate, associated to the decreased formation of acetic acid, whose selectivity drops earlier in experiment E than in experiment D, suggests that surface acetate species (which give rise to desorption of acetic acid at high water surface concentration [16]) tend to decompose at low surface water concentration. On the other hand, the relative ratios of selectivities to CO, CO_2 and CH_4 does not change very much in experiments E and D.

To have more information on the role of the different C-containing products, we performed experiments at different contact times. To do this, water-to-ethanol feed ratio of six was used. This has been done by varying the feed flow rate using the same catalyst bed containing 0.27 g of quartz and 0.03 g of catalyst. The data reported in Figs. 1 and 2 refer to experiments performed at 723 K. It is evident that by increasing contact time the conversion of ethanol increases significantly at this temperature as expected indeed. By increasing contact time, the acetic acid selectivity decreases progressively, while the selectivities to CO_2, to diethylether and to acetone increase progressively. In particular, at the higher contact times, diethylether becomes the main C-containing product. The selectivities to diethylether and CO_2 increase more than that to acetone at longer contact times, while at the highest contact times also acetaldehyde starts to be observed among the products, together with CO and methane. On the contrary, the selectivity to ethylene seems to be poorly sensitive to contact time.

The reaction of formation of diethylether and acetic acid are necessarily parallel reactions, according to stoichiometry. Thus, the increased formation of diethylether with respect to acetic acid upon varying contact time must again be explained as an evidence of external mass transfer limitations. Acetic acid formation is likely

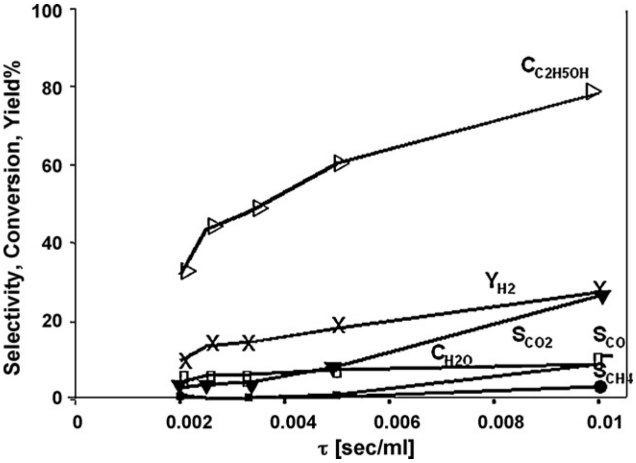

Fig. 1. Conversion/selectivity/yield (%) vs. contact time of ethanol steam reforming over NiZnAl catalysts at 723 K (83.1% He; 2.4% CH_3CH_2OH; 14.5 H_2O; $W_{cat} = 0.015$ g): ×, H_2 (Y); ●, CH_4 (S); –, CO (S); ▾, CO_2 (S); ▹, C_2H_5OH (C), □, H_2O (C).

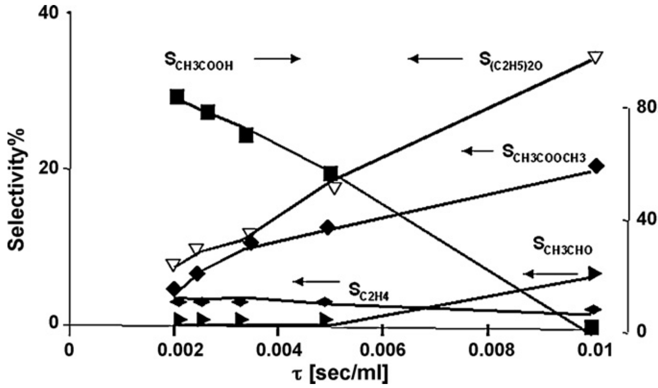

Fig. 2. Selectivities (%) vs. contact time of ethanol steam reforming over NiZnAl catalysts at 723 K (83.1% He; 2.4% CH_3CH_2OH; 14.5 H_2O; $W_{cat} = 0.015$ g): ×, H_2 (Y); ●, CH_4 (S); –, CO (S); ▼, CO_2 (S); ♦, C_2H_4 (S); ►, CH_3CHO (S); ■, CH_3COOH (S); ★, $(C_2H_5)_2O$ (S); ▷, C_2H_5OH (C).

favoured at lower contact times as an effect of increased water surface concentration at higher reactants flow rates. On the contrary, diethylether formation is again favoured at lower reactants flow rates (higher contact times) as an effect of decreased water surface concentration. On the contrary, the favoured production of CO_2 and acetone at the expense of acetic acid may be due to the role of acetic acid as an intermediate in the formation of these compounds.

We also looked at the product distribution at higher temperature. In Figs. 3 and 4, the product distributions observed at 813 and 1103 K, respectively, are reported as the function of contact time. At both these temperatures, ethanol conversion is complete and only one-carbon atom products are observed together with hydrogen. The experimental values are compared with the calculated values expected if thermodynamic WGS and MSR equilibria were established. At 820 K, the CO_2 and CH_4 product concentration are higher then forecasted by thermodynamics while CO and hydrogen concentration are lower. The product concentration does not change very much with contact time in this range. These data suggest that WGS and MSR equilibria are not established even at the highest contact time, thus the product distribution being mainly governed by kinetics and may be affected by diffusion limitations. On the other hand, we note that the $(CO_2 + CO)/CH_4$ ratio is very high (near 9).

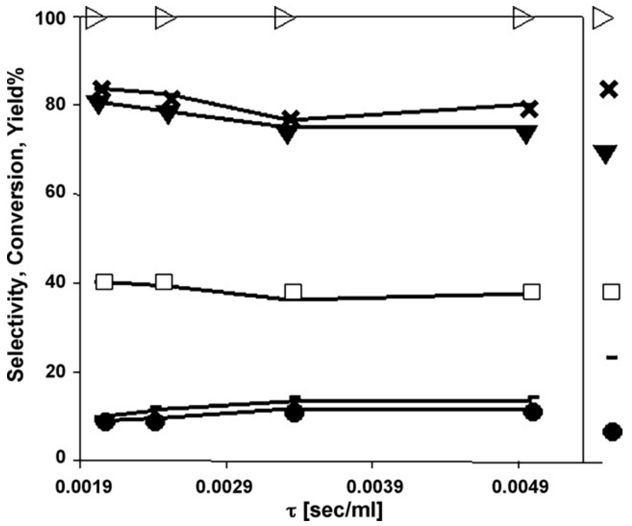

Fig. 3. Conversion/selectivity/yield (%) vs. contact time of ethanol steam reforming over NiZnAl catalysts at 813 K (83.1% He; 2.4% CH_3CH_2OH; 14.5 H_2O; $W_{cat} = 0.015$ g): ×, H_2 (Y); ●, CH_4 (S); –, CO (S); ▼, CO_2 (S); ▷, C_2H_5OH (C), □, H_2O (C). On the right calculated thermodynamic values.

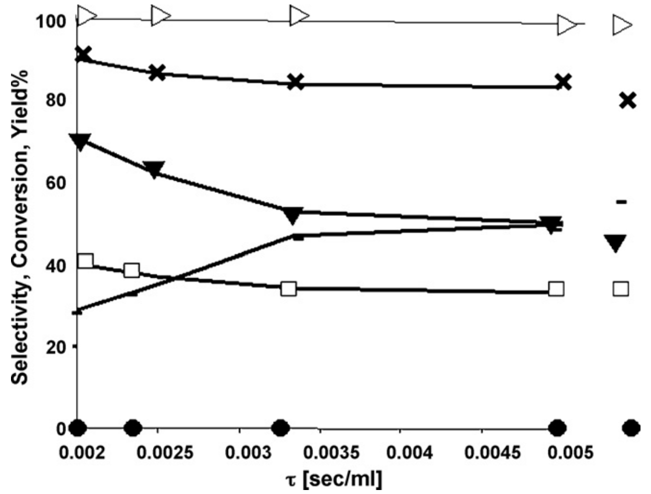

Fig. 4. Conversion/selectivity/yield (%) vs. contact time of ethanol steam reforming over NiZnAl catalysts at 1103 K (83.1% He; 2.4% CH_3CH_2OH; 14.5 H_2O; $W_{cat} = 0.015$ g): ×, H_2 (Y); ●, CH_4 (S); –, CO (S); ▼, CO_2 (S); ▷, C_2H_5OH (C), □ H_2O (C). On the right calculated thermodynamic values.

At 1103 K already at the lowest contact times CH_4 selectivity is very low, as expected by thermodynamics. However CO_2 and H_2 concentration are definitely higher than expected by thermodynamics while CO concentration is definitely lower. On the other hand, by increasing contact time the concentration tends towards the thermodynamic value. These data provide a proof that CO_2 is mostly an earlier product with respect to CO and that at high temperature the reverse water gas shift reaction occurs, together with MSR, as already reported [21].

To evaluate the role of acetic acid an intermediate in ESR, we also studied the steam reforming of acetic acid in similar conditions (Fig. 5). At 730 K, acetic acid starts to be converted producing acetone as CO_2, thus confirming the role of acetic acid as an intermediate. Note that the selectivity calculated here is based on carbon atoms. The molar ratio between acetone and CO_2 is indeed 1 (selectivities are calculated on carbon atom basis), as expected by the stoichiometry of the ketonization reaction:

$$2CH_3COOH \rightarrow CH_3COCH_3 + H_2O + CO_2 \quad (2)$$

At 830 K, the selectivity to acetone concentration falls to zero, with the corresponding production of CO, CO_2 methane and hydrogen. The $(CO_2 + CO)/CH_4$ and CO_2/CO ratios are very high. This suggests

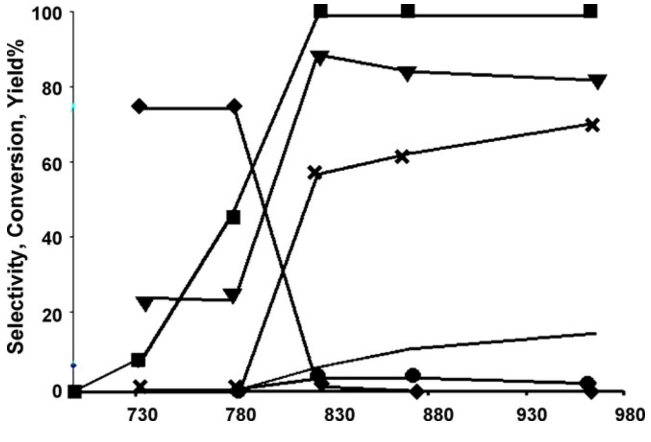

Fig. 5. Conversion/selectivity/yield (%) vs. temperature of acetic acid steam reforming over NiZnAl catalysts (total flow rate 300 ml/min, 83.5% He, 2.6% CH_3COOH, 13.9% H_2O; $W_{cat} = 0.03$ g): ×, H_2 (Y); ●, CH_4 (S); –, CO (S); ▼, CO_2 (S); ♦, CH_3COCH_3 (S); ■, CH_3COOH (C).

that, in this range, acetic acid gives rise not only to its decomposition/decarboxilation:

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad (3)$$

but also to a complete reforming, with a predominant formation of CO_2

$$CH_3COOH + 2H_2O \rightarrow 2CO_2 + 4H_2 \quad (4)$$

It seems interesting to remarks that, according to our calculations, above 830 K the CO, CO_2, H_2 and H_2O concentrations correspond closely to those expected by thermodynamics of WGS. On the contrary, it is evident that MSR is far from equilibrium, on the CH_4-rich side.

4. Discussion

These data reported here confirm that two main regimes exist for the ESR reaction over Ni–Zn–Al catalysts. The limit between the two regimes, in the range 700–850 K in our conditions, depends on reaction conditions. Above the limit ethanol conversion is total, acetaldehyde is detected among the products only if water inlet concentration is relatively low (e.g. at the stoichiometric water-to-ethanol ratio of 3). With water excess, only one-carbon atom products (CH_4, CO and CO_2) are observed. As already discussed [16] (and further confirmed here) the composition in this regime tends to the equilibrium composition (WGS and MSR, equilibria) by increasing contract time and temperature, as well as by increasing catalyst surface area, coming to the equilibria from the CH_4-rich side for MSR e from the CO_2-rich side for WGS (i.e. through reverse-WGS). In this regime, obviously, the larger the water concentration, the higher hydrogen and CO_2 yield. These data confirm that methane arises from decomposition of two-carbon atom containing species, methanation being not relevant in our conditions.

Below the above temperature limit, multiple carbon atoms products (acetic acid, acetaldehyde, acetone, ethylene and diethylether) are predominant. The data show that the main product in our conditions, at low temperature and conversion is acetic acid, produced by the following reaction:

$$C_2H_5OH + H_2O \rightarrow CH_3COOH + 2H_2 \quad (5)$$

Our data suggest that the kinetics of this reactions has negative order in ethanol and likely positive order in water.

As shown both by ethanol steam reforming experiments and by acetic acid steam reforming experiments, acetic acid converts into acetone by ketonization above 700 K through reaction (2) and, at higher temperatures, decomposes into CH_4 and CO_2 and CO. The $(CO + CO_2)/CH_4$ ratio obtained is much higher than 1, namely near 10, and this implies that acetic acid only in part may decompose through reaction (3), likely with the intermediacy of surface acetate species [16]. This is the methane forming step in our conditions.

However, acetic acid is predominantly totally steam reformed through reaction (4). This is a central topic in ESR path, and merits a larger discussion. In fact, this step resulting in methane formation, strongly influences the hydrogen productivity: the larger the formation of methane, the lower the selectivity to hydrogen. Alternatively, higher temperatures are needed to steam reform methane formed here, with the drawback of going to a region where WGS equilibrium is less favourable.

Previous spectroscopic studies showed that acetate species are formed during ESR over Ni catalysts including that used here [13,15,16] and that these species may decompose producing methane and CO. On the other hand, it has also been shown that acetate species are intermediates in ethanol oxidation over metal oxide catalysts such as vanadia–titania [24] and manganese oxides on alumina [25]. In these cases, according to the Mars–van Krevelen or redox mechanism [26], the oxidized catalyst center is the true oxidant, i.e. oxidized vanadium and manganese oxide species, respectively, and O_2 that reoxidizes the catalyst.

Steam reforming is, at least formally, a similar oxidation reaction where the oxidant is water. Our characterization studies allowed us to conclude that the redox state of dispersed Ni in ESR catalysts is quite labile, water acting easily as an oxidant for Ni metal centers to Ni^{2+} [27]. This reaction is possible not only for isolated atomic nickel but also at defects or at the surface of Ni metal particles. A redox mechanism has been proposed also for water gas shift reaction on Ni based catalysts [28]. It is possible to suppose that part of acetate species (either formed by acetic acid dissociative adsorption or by ethanol adsorption and oxidation [16]), may be fully burned by Ni oxide species formed by oxidation of Ni metal centers by water giving rise essentially to CO_2 and H_2. This should be the CO_2 forming step we considered as unknown in our previous work [16].

In the low temperature/low conversion regime, diethylether and ethylene are also formed. They are certainly the products of parallel reactions with respect to the acetic acid formation reactions.

$$C_2H_5OH \leftrightarrows C_2H_4 + H_2O \quad (6)$$

$$2C_2H_5OH \leftrightarrows (C_2H_5)_2O + H_2O \quad (7)$$

Experiments performed varying contact time and reactants flow rate show that diethylether formation is favoured by increasing surface ethanol concentration and by decreasing water surface concentration.

As said, acetaldehyde formation is favoured at higher ethanol concentrations, low reactants flow rate, low water-to-ethanol ratio. This is likely due to the competition of the acetaldehyde formation reaction

$$C_2H_5OH \rightarrow CH_3CHO + H_2 \quad (8)$$

or, better, of the desorption of adsorbed acetaldehyde with the acetic acid formation reaction (5), which probably implies adsorbed acetaldehyde as an intermediate and needs water as a reactant.

5. Conclusions

Experiments performed over a NiZnAl catalyst in different flow conditions show that:

1. Acetaldehyde is an intermediate of ESR in its adsorbed form, but is converted into surface acetate species which give rise to desorption of acetic acid if water-to-ethanol feed ratio is sufficiently high (experiments 5.5–6). In excess water acetaldehyde is not formed among the products.
2. Acetic acid and surface acetate species (adsorbed acetic acid) are very likely the key intermediates in ethanol steam reforming. The formation rate of acetic acid from ethanol and water at low temperature and conversion has a negative reaction order on ethanol concentration and a positive one on water concentration.
3. In the presence of excess water acetic acids gives rise to acetone + CO_2 at low conversion, and is steam reformed at high conversion, giving rise to hydrogen and $(CO + CO_2)/CH_4$ ratios near 10.
4. During ESR, above 700 K part of acetate species decompose and this represents the methane forming step of ESR.
5. If excess water is fed, most of acetate species are converted into CO_2 possibly through an oxidation step. Water likely oxidizes Ni centers that burn acetate species.
6. Acetone, which is formed by ketonization of acetic acid, may also play a role of intermediate in the conversion of acetic acid into CH_4, CO, CO_2 and H_2.

7. Above 800 K, the reaction product distribution (CH_4, CO, CO_2 and H_2) tends to WGS and MSR thermodynamic equilibria. This occurs through reverse-WGS and direct MSR. Methanation does not occur in our conditions.
8. Hydrogen yields as high as 95% have been obtained by ESR over NiZnAl catalyst at 853 K.

Acknowledgement

The authors acknowledge funding from MIUR-PRIN (2007-8). The collaboration of Ing. Flavio Ferdinando is acknowledged.

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